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Evaluating Humidity and Sea Salt Disturbances on CO_2 Flux Measurements

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ABSTRACT

Global oceans are an important sink of atmospheric carbon dioxide (CO_2). Therefore, understanding the air–sea flux of CO_2 is a vital part in describing the global carbon balance. Eddy covariance (EC) measurements are often used to study CO_2 fluxes from both land and ocean. Values of CO_2 are usually measured with infrared absorption sensors, which at the same time measure water vapor. Studies have shown that the presence of water vapor fluctuations in the sampling air potentially results in erroneous CO_2 flux measurements resulting from the cross sensitivity of the sensor. Here measured CO_2 fluxes from both enclosed-path Li-Cor 7200 sensors and open-path Li-Cor 7500 instruments from an inland measurement site are compared with a marine site. Also, new quality control criteria based on a relative signal strength indicator (RSSI) are introduced. The sampling gas in one of the Li-Cor 7200 instruments was dried by means of a multitube diffusion dryer so that the water vapor fluxes were close to zero. With this setup the effect that cross sensitivity of the CO_2 signal to water vapor can have on the CO_2 fluxes was investigated. The dryer had no significant effect on the CO_2 fluxes. The study tested the hypothesis that the cross-sensitivity effect is caused by hygroscopic particles such as sea salt by spraying a saline solution on the windows of the Li-Cor 7200 instruments during the inland field test. The results confirm earlier findings that sea salt contamination can affect CO_2 fluxes significantly and that drying the sampling air for the gas analyzer is an effective method for reducing this signal contamination.

1. Introduction

Global oceans are an important sink of atmospheric carbon dioxide (CO_2). Therefore, understanding the air–sea flux of CO_2 is a vital part in a correct description of the global carbon balance. The air–sea flux of CO_2 (F_{CO_2}) is controlled by the difference in partial pressure of CO_2 in the water and in the air (ΔpCO_2) and the transfer velocity k, and is often expressed as

$$F_{CO_2} = K_0 k \Delta pCO_2, \qquad (1)$$

where K_0 is a gas specific solubility constant and k is a measure of the efficiency of the gas transfer over the water–air surface. Instead of calculating the flux of CO_2 with Eq. (1), the flux can be directly measured with the eddy covariance (EC) technique. EC measurements have been frequently used to study CO_2 fluxes over both land and ocean. Over land the magnitude of CO_2 fluxes are generally larger during daytime conditions compared to over the ocean, which can make ocean-based EC measurements more sensitive to errors, including cross sensitivities of the gas analyzer. However, in continental places there are also great difficulties sometimes in complex heterogeneous terrain with variations that can fall within the sensitivity range of instruments, making concerns largely site specific.

Cross sensitivity is defined here as an observed change in CO_2 density caused by a change in water vapor density. In this study we consider cross sensitivity to water

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vapor after processing CO_2 fluxes to account for IR density variations. Temperature sensitivity related to CO_2 flux retrieval is not investigated here. Open ocean studies have shown that measuring CO_2 density when water vapor density is changing in the sampling air can give erroneous CO_2 measurements as a result of cross sensitivity (Kohsiek 2000; Kondo et al. 2014; Landwehr et al. 2014; Blomquist et al. 2014).

According to a study by Kohsiek (2000) in which two gas analyzers were compared (NOAA and KNMI sensors), the two most likely explanations for the cross-sensitivity problem are the pressure band broadening effect and the effect of the presence of liquid water in the optical path. Commercially used sensors, such as LI-7200 and LI-7500 (from Li-Cor Inc., Lincoln, Nebraska) have, according to the manufacturers, corrections for the pressure broadening effect incorporated into their software. However, according to Kondo et al. (2014), the corrections introduced by the manufacturers were not enough and consequently the instruments could overestimate the CO_2 mixing ratio and the magnitude of the flux.

It is notable that all studies showing high-cross-sensitivity errors in the CO_2 fluxes are open ocean or coastal sea studies. Even after following the calculations of Webb et al. (1980), the CO_2 fluxes from open-path and enclosed-path instruments can be an order of magnitude higher than expected values based on typically accepted bulk flux parameterizations (Prytherch et al. 2010; Landwehr et al. 2014). Landwehr et al. (2014) showed that a postprocessing correction method, which was suggested by Prytherch et al. (2010) [Peter K. Taylor (PKT) corrections], could not be used to correct the CO_2 fluxes and instead supported the conclusions of Miller et al. (2010) that an order-of-magnitude bias in the measured CO_2 fluxes could be removed only if the sample air is dried. Landwehr et al. (2014) found that the CO_2 flux estimates from the dried and undried Li-Cor sensors agreed for very low ambient latent heat fluxes ($<7\,\mathrm{W\,m^{-2}}$). The terminology of *dried sensor* for both Landwehr et al. (2014) and this study means that the intake sample airstream has been passed through a Nafion dryer that effectively removed fluctuations of water vapor before the airstream is passed to the gas analyzer. The practical recommendation of Miller et al. (2010), Landwehr et al. (2014), and Blomquist et al. (2014) would be to use closed or enclosed-path instruments with a diffusion dryer to remove water vapor fluctuations for EC flux measurements of CO_2 over the open ocean.

Blomquist et al. (2014) showed convincingly that the measured mean CO_2 concentration can be several parts per million (ppm) different if a Nafion air dryer is used. From the studies by Kondo et al. (2014) and Blomquist et al. (2014), it is less clear to what extent the actual CO_2 fluxes are changing significantly by drying the air. Neither of these studies focused specifically on the fluxes, although Blomquist et al. (2014) discussed, based on their analysis, that errors in the CO_2 flux of about 10% of the specific humidity may be possible. By recomputing CO_2 from the raw absorbances with an adjustment of a water crosstalk constant ($a_w = 1.7$ instead of 1.15), Blomquist et al. (2014) showed a large removed offset in measured CO_2 concentration in moist air. However, Blomquist et al. (2014, p. 261) also commented that ''recomputing fluxes for the period without the dryer from the corrected time series did not yield a significant improvement in flux variance and bias.'' A study more directly focusing on the effects of drying the air and how it affects measured CO_2 fluxes rather than the level of CO_2 concentration is therefore complementary to existing published literature.

Spectral attenuation or high-frequency flux loss is an additional issue for all eddy covariance measurements because they are bandwidth limited (Blomquist et al. 2014). Resolution of the smallest eddies (highest frequencies) is limited by sensor separation, sampling frequency, and low-pass filtering from tubing in closed and enclosed-path systems. Correction for this effect is not the focus here but two general approaches to perform spectral attenuation corrections are using transfer functions (Moore 1986; Horst 1997; Massman 2000) and spectral similarity methods (Hicks and McMillen 1988). The spectral attenuation corrections are better described and are not as large as the magnitude order errors discussed for oceanic flux experiments.

An additional concern for the ocean flux community is the presence of hygroscopic deposits on the optics of CO_2 gas analyzers, such as sea salt, which could also affect the measurements (Kondo et al. 2014). Blomquist et al. (2014) discussed that if hygroscopic contamination is a major factor inducing cross sensitivity, then the magnitude of cross correlation between water vapor and CO_2 should decrease following a wash cycle on their LI-7500 analyzer, which they did not observe. They therefore argued that optical contamination may not have been the source of additional cross correlation in their case, or perhaps that the relevant contaminants are resistant to removal by rinsing. It is also possible that the saltwater films on the sensor lenses recover too fast after washing (within minutes) to allow the observation of a ''clean'' flux signal, which is typically computed over time scales of 10 min to 1 h. In the context of determining an appropriate eddy covariance flux that relates to the dynamic and turbulent scales of the atmospheric boundary layer, it is appropriate to use stationarity tests. A common approach to determine a nonfixed averaging time includes using ogive curves to assure that extending the cross covariance integral does not add significantly more than 95% for the flux within each chosen averaging period.

A third concern in the flux community for both land and ocean studies is that when using open-path sensors, surface heating from the instrument itself could lead to warming of the air in the measuring path and to errors in the CO_2 fluxes, which will not be corrected by the density corrections because normally the temperature used in the density correction is not measured directly in the measuring path of the gas analyzer (Burba et al. 2008). The third issue is substantial only in very cold climates. Wang et al. (2016) compared spectroscopic temperature sensitivity to the self-heating issue and found no evidence for self-heating as the cause of a probable uptake CO_2 flux artifact. The temperature range studied in Wang et al. (2016) was from about −20° to +25°C. Our study will provide field measurement results on the former issues of water vapor and sea salt. In the case of measurements on ships, there are several additional concerns related to ship motion and airflow distortion not further addressed here—see instead for instance Blomquist et al. (2014), Prytherch et al. (2015), and Landwehr et al. (2015).

Here we aim to investigate possible disturbances by water vapor and salt contamination on turbulent fluxes and respond to two main questions, Does drying the air influence measured CO_2 fluxes, and will measured CO_2 fluxes be affected by sea salt contamination on the windows of instruments? We discuss some results as they are presented in section 3 and also summarize our recommendations for measuring turbulent fluxes of CO_2 with infrared gas analyzers in our summary and conclusions sections.

2. Sites, measurements, and data processing

Field measurements were conducted at an agricultural site, Marsta, located close to Uppsala, Sweden (Halldin et al. 1999). The period from April to June 2015 is used as the main dataset in this study. This is complemented by a more limited set of measurements from the Östergarnsholm marine field site located on a small island in the Baltic Sea. These measurements were conducted during the summer of 2015 (July–September).

a. Field measurements from Marsta

In Marsta two open-path Li-Cor 7500 gas analyzers and two enclosed-path Li-Cor 7200 instruments were mounted next to one Gill WindMaster sonic anemometer at a measurement height of 7 m (see Fig. 1). To minimize the loss of measured high-frequency fluctuations, the length of the intake tubes was kept at about

FIG. 1. A picture of the instrument setup with four Li-Cor instruments and the Gill sonic anemometer at the field measurement site Marsta near Uppsala.

0.5 m. The inner diameter of the tubes was 5 mm and a flow rate of 18 L min^{-1} was used. The distance between the instruments were kept as short as possible (maximum 40 cm), and the scalar sensors were placed slightly below the anemometer, consistent with recommendations to minimize flux loss caused by sensor displacement (Horst and Lenschow 2009; Nilsson et al. 2010). The agricultural landscape surrounding the site is very flat, and in some wind direction sectors the upwind fetch is undisturbed crop fields for 4–5 km.

There was very low vegetation for most of the period as it was in the beginning of the growing season. Local farmers nearby noted, however, an unusually early start of their spring activities in 2015 (with fertilization of the fields beginning around 12 April and spring seeding completed about 2–3 weeks later). This was mainly related to April being very dry (only about 10 mm were recorded, which is about one-third of the normal precipitation) and warmer than normal (6.8°C compared to 4.0°C for the climatic period of 1961–90). In May 2015 in contrast the mean temperature was close to normal (9.6°C compared to 10.2°C as a mean value for the period 1961–1990) and there were much more precipitation, about 85 mm—almost 3 times more than normal. These different conditions are mentioned here because data from these two months were used to determine a reasonable selection criteria in our quality control of CO_2 fluxes. In June 2015 we had 16 days with precipitation, but only 1 day with more than 10 mm. The monthly precipitation was only marginally less (1 mm) than the climatic mean value of 45 mm for the period 1961–90, and the monthly mean temperature was 14°C, which is 1°C cooler than normal.

The field measurements from Marsta were divided into four periods, which correspond to

FIG. 2. A picture of the 30-m tower at the Östergarnsholm site with the 10-m level indicated. Also seen is a smaller tower instrumented for measurements of marine aerosols.

1) Measurements in April, when all four Li-Cor instruments were used in a reference setup, with no drying of intake air and no influence from an external source of salt.
2) Measurements in May, when one of the enclosed-path Li-Cor 7200 instruments (called Li72b) had a Nafion membrane dryer (PD-200T) mounted to remove water vapor fluctuations. For more details on the application of this dryer system in the context of marine measurements of CO_2 fluxes, refer to Landwehr et al. (2014).
3) Measurements in June, which had the same setup as in period 2, which is used as a reference for the sea salt experimental field test.
4) Measurements in June, with a smaller amount of data for which the enclosed-path Li-Cor 7200 instruments (with and without the Nafion dryer) was sprayed with a saline solution to mimic the effect of sea salt contamination on the instrument windows.

This division of data into these four periods—periods 1–4, respectively—was done to perform tests of the separate effects of drying the air, to investigate the sea salt contamination issue, and to compare potential differences in measured fluxes in the reference setup(s).

b. *Field measurements from Östergarnsholm*

Field measurements were also conducted at the Swedish marine Integrated Carbon Observation System (ICOS) site Östergarnsholm. This site is located on the island Östergarnsholm, 4 km from the eastern coast of the larger island Gotland in the Baltic Sea. The southern part of the island is very flat and rises only a couple of meters above sea level. A 30-m instrumented tower is located here (see Fig. 2), which has been used for measuring CO_2 fluxes and atmospheric turbulence and mean parameters semicontinuously for the past 20 years (Rutgersson et al. 2008; Högström et al. 2008).

During the period between July and September 2015, two Li-Cor 7200 instruments and one Li-Cor 7500 instrument were mounted close to a CSAT sonic anemometer at a nominal measurement height of 10 m MSL. Only data with wind from the 80°–220° sector were used to ensure the measured fluxes represent sea conditions.

The instrumental setup was essentially identical to that of period 2 in Marsta but only one Li-Cor 7500 instrument was used. One of the Li-Cor 7200 instruments had a Nafion dryer installed to remove water vapor fluctuations, whereas the other Li-Cor 7200 was left in a standard operating mode measuring both CO_2 fluxes and latent heat fluxes.

c. *Overview of encountered environmental conditions and CO_2 fluxes at the two sites*

To make a brief comparison of the conditions at the two sites, we list in Table 1 the mean, maximum, and minimum values of wind speed, temperature, and humidity, as well as quality-controlled fluxes of CO_2. If we compare the conditions at the two sites during the time of deployments, we had larger diurnal cycles at Marsta compared to Östergarnsholm. The lowest temperature in Marsta of −0.3°C also came in early spring and the highest value of 27.8°C was in June. At Östergarnsholm

TABLE 1. Mean, maximum, and minimum of meteorological parameters and the flux of CO_2 (two different units) at Marsta during April–June 2015 and at Östergarnsholm during July–September 2015.

Site	Wind speed (m s^{-1})	Temp (°C)	Humidity (g kg^{-1})	CO_2 flux (ppm m s^{-1})	CO_2 flux (μ mol m^{-2} s^{-1})
Marsta (mean)	2.5	12.9	5.2	−0.050	−2.1
Östergarnsholm (mean)	6.8	18.1	8.9	−0.004	−0.16
Marsta (max)	8.5	27.8	9.0	0.173	7.2
Östergarnsholm (max)	13.7	23.2	13.9	0.012	0.50
Marsta (min)	0.1	−0.3	0.5	−0.579	−23.0
Östergarnsholm (min)	0.4	12.8	1.4	−0.019	−0.79

the observed temperature range was not as large, ranging from 12.8° to 23.2°C, and had a mean value of 18.1°C, which can be compared with the mean value at Marsta, which was 12.9°C. The wind speed was higher for Östergarnsholm with a mean value of 6.8 compared with 2.5 m s^{-1} at Marsta, and the highest hourly wind speed was 13.7 m s^{-1} at Östergarnsholm, whereas it was 8.5 m s^{-1} at Marsta. This is a general observation for the coastal site compared to the inland site, that it is windier at Östergarnsholm. Higher humidity is also generally found at the marine site compared to the inland site with differences of 3.7 g kg^{-1} in the mean for the periods considered. In fact, the maximum value at Marsta for the considered periods was 9.0 g kg^{-1}, which is comparable to the mean value at Östergarnsholm, which was 8.9 g kg^{-1}.

When it comes to the range of encountered CO_2 fluxes, the values reported in Table 1 refer to fluxes that have undergone visual inspection and quality control in a number of steps, which will be described in more detail later in this paper. Here, however, we first want to give an overview of the magnitudes encountered at these two sites, which are indeed very different from each other. The mean flux at the inland agricultural site was $-2.1\,\mu$mol $m^{-2}\,s^{-1}$, which is more than 13 times larger than the mean flux at the marine site. The range of observed fluxes at Marsta was from 7.2 to $-23.0\,\mu$mol $m^{-2}\,s^{-1}$, which is quite comparable to the ranges discussed for instance in Baldocchi et al. (2001) when comparing an Italian CarboEuroFlux site with the AmeriFlux reference (their Fig. 2). For Östergarnsholm the mean value of $-0.16\,\mu$mol $m^{-2}\,s^{-1}$ or about -5.0 mol $m^{-2}\,yr^{-1}$ corresponds well to previous estimates of air–sea exchange of CO_2 at the site for the month of August presented by Rutgersson et al. (2009). A smaller flux and a range of fluxes between 0.5 and $-0.79\,\mu$mol $m^{-2}\,s^{-1}$ was thus observed at Östergarnsholm compared to Marsta. For more detailed discussions on estimates of CO_2 exchange in coastal zones and inland areas, refer to Grachev et al. (2011), which showed similar magnitudes of averaged CO_2 turbulent flux over the Gulf of Mexico of -7.47 mol $m^{-2}\,yr^{-1}$ but very different results over suburban areas. Different results with an average CO_2 flux from the ocean to the atmosphere of 3.9 mol $m^{-2}\,yr^{-1}$ has also been reported for open ocean conditions in the equatorial Pacific (McGillis et al. 2004). Different marine areas show different results also depending on the season, but the magnitude of fluxes are often lower than at many sites over land.

In Table 1 we have listed CO_2 fluxes in both μmol $m^{-2}\,s^{-1}$ and ppm m s^{-1} for the convenience of readers used to specific units. For the instrument comparison we choose to use ppm m s^{-1}, as it is a convenient unit to use when studying kinematic CO_2 flux when vertical wind speed is measured in meters per second and CO_2 is in parts per million. Positive flux values denote upward fluxes (CO_2 respiration), and negative values correspond to downward fluxes (CO_2 photosynthesis).

d. Data processing

In this paper the main focus is on the quality and practical issues with CO_2 flux measurements using the eddy covariance technique. We used a fixed time-averaging period of 10 min throughout this paper, but we also performed the analysis for 1-h averaging periods with no difference in our main results. Following Sahlée et al. (2008) the mass fluxes for CO_2 and latent heat are

$$F_{CO_2} = F_C = \rho_d \overline{w'c'}, \quad \text{and} \tag{2}$$

$$F_v = \rho_d \overline{w'q'}. \tag{3}$$

Here w denotes the vertical wind, q is the mixing ratio of water vapor, c is the mixing ratio of CO_2 relative to dry air, and ρ_d is the density of dry air. The usual notation is used in the Reynolds decomposition, that is, an overbar denotes a mean value and the prime denotes a deviation from the mean value. The direct conversion (DC) method is used to convert from molar densities of CO_2 and humidity relative to the ambient air, which is measured by the infrared gas analyzers, to mixing ratios. This is described in detail in Sahlée et al. (2008). The vertical fluxes of CO_2 and water vapor using the DC method are equal to the corrected fluxes using Webb et al. (1980) as shown in Sahlée et al. (2008). Please note that we use the same vertical wind signal—w—in all the flux calculations and hence the difference in the results is related only to differences in measured CO_2 and humidity signal between the instruments. For the sake of completeness, some more details on the data processing are described. Fluxes were calculated in a rotated coordinate system, using natural wind coordinates, with double rotation following procedures described in Kaimal and Finnigan (1994). Despiking was not initially applied because outliers seemed to be effectively removed by our other quality control criteria based on relative signal strength, which is to be described later. Some suspicious data were, however, removed based on instrumental error flags (i.e., phase lock error) and when the Li-Cor 7500a and 7500b instruments sporadically differed more than 0.05 ppm m s^{-1}. A procedure that has little consequence for the comparisons with the Li-Cor 7200 is shown in the appendix (Figs. A3a and A3b). Hence, this additional filtering is not important for the evaluation of the effects caused by drying the intake airstream or the sea salt disturbances.

The choice of 10 min as an averaging period was for quality-controlled data, which were also checked as corresponding to an approximate range of frequencies between 1/1000 and 3/1000 Hz, where the flux

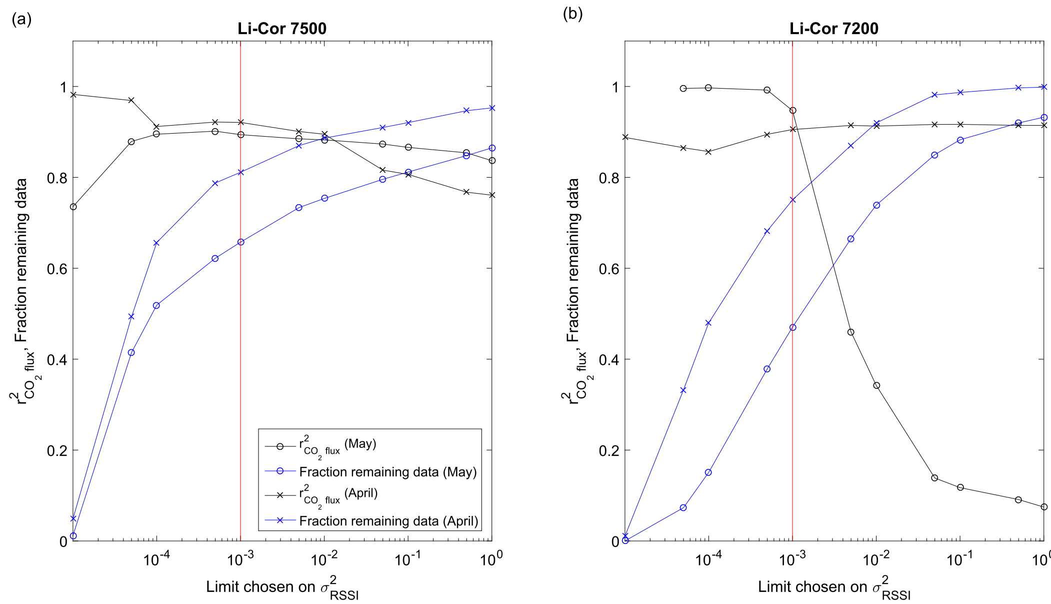

FIG. 3. The squared correlation coefficient for the CO_2 flux ($r^2_{CO_2}$, black), and the fraction of remaining data (blue) is shown as a function of different threshold limits for the variance of the RSSI value (σ^2_{RSSI}). The result for the (a) two Li-Cor 7500 instruments and (b) two Li-Cor 7200 instruments. Data from April 2015 (lines with crosses) and May 2015 (lines with circles). The threshold limit $\sigma^2_{RSSI} = 0.001$ is denoted (vertical red line).

contribution was smaller compared to higher and lower frequencies. Such a cospectral ''gap'' separated what we considered to be the turbulent flux range from more low-frequency correlations. The choice of the 10-min averaging time is used here to stabilize the observations of CO_2 fluxes rather than calculating a final flux value that can be attributed to specific surface characteristics. Also, the spectral slope of the vertical wind components was checked, and the overall behavior of CO_2 spectra and cospectra from all the instruments was checked manually. No frequency corrections for loss of variance or flux were performed, as this was not the focus of the current investigation. We consider the approach taken as sufficient to evaluate the effect of drying and the effect of sea salt on CO_2 fluxes. Additional processing may be necessary if attribution of measured fluxes to specific surfaces are desirable. In such a case, further review of data processing details may be needed (Lee et al. 2005; Nakai et al. 2006; Starkenburg et al. 2016), including flux footprint modeling (Kljun et al. 2004; Vesala et al. 2008).

3. Results and discussion

We present our results in three subsections. To meet an acceptable data quality, we selected thresholds on the quality indicators and this procedure is presented first. Second, we present the results from field tests of drying the air to remove water vapor fluctuations. These include data from both Marsta, the agricultural site, and Östergarnsholm, the marine site. Finally, we present results about sea salt contamination.

a. Quality control

The gas analyzers give a signal strength index called relative signal strength indicator (RSSI), which was saved for all our instruments at high frequency (20 Hz). This can be used either as a quality control measure by itself or used to form additional quality control parameters. We noted that the RSSI value itself could differ systematically between instruments, which is typical between instrument brands. Sometimes they differed by a near constant under very good conditions with no rain or other disturbances. Therefore, from 10-min mean values of RSSI it was difficult to choose a specific value that would separate the high-quality data from the lower-quality data and at the same time not remove too much data (see the appendix). Instead we choose the variance of RSSI (σ^2_{RSSI}) to be determined for each 10-min period, to be a more useful tool to indicate whether the data are of high or low quality. The threshold value is thus to be selected.

The squared correlation coefficient for the CO_2 flux (black lines) from the two Li-Cor 7500 instruments in Fig. 3a and for the two Li-Cor 7200 instruments in Fig. 3b is shown as a function of different threshold values chosen for the variance of the RSSI value. Also shown is the fraction of remaining data using different threshold values (blue) and the threshold value

$\sigma^2_{\mathrm{RSSI}} = 0.001$ (vertical red line), which is the level chosen in this paper to assure high-quality data. Any 10-min period with a higher variance of RSSI than this is considered of less than acceptable quality, since the correlation and agreement between instruments diminish if a less strict limit is chosen. The data from April are marked with crosses and those from May with circles. Although defining a threshold limit for acceptable data quality mainly based on correlation measures and agreement between separate instruments includes some subjectivity, this was the chosen approach for this study.

In May with many rain events (it rained 22 out of 31 days) and with the introduction of the Nafion dryer on one of the Li-Cor 7200 instruments, the squared correlation coefficient for the CO_2 fluxes from the two Li-Cor 7200 instruments dropped to low values (far below 0.8) when a less strict threshold value was chosen. Similar results were also found for data in June. The appendix shows (Fig. A1) that the drop in the correlation coefficient occurred between the dried Li-Cor 7200b and Li-Cor 7500 instruments but not between the enclosed-path sensors. This indicates the risk in accepting data from dried sensors with a threshold limit set higher than 0.001. Selecting a good quality control parameter and threshold value is of course not trivial, and using the appendix (Figs. A2–A4) we discuss and compare our choices to another criteria based on instead choosing a limit for RSSI values scaled with their median RSSI value ($\mathrm{RSSI}/\widetilde{\mathrm{RSSI}}$). The median was determined for each period, which essentially means a monthly median of all the 10-min values. Based on that analysis, we consider the σ^2_{RSSI} parameter preferable.

From the choice of a threshold limit of $\sigma^2_{\mathrm{RSSI}} = 0.001$, we keep roughly 81% of the measured Li-Cor 7500 data in April and 66% in May. For the Li-Cor 7200 data, the acceptable available data are a little lower, with about 75% in April and 47% in May.

b. *Does drying the air influence measured CO_2 fluxes?*

1) MARSTA

From period 1 and the field experiments in Marsta, there were 2044 high-quality data (10-min values) remaining with our chosen threshold value of $\sigma^2_{\mathrm{RSSI}} < 0.001$ and $|F^{(\mathrm{Li75b})}_{CO_2} - F^{(\mathrm{Li75a})}_{CO_2}| < 0.05\,\mathrm{ppm\,m\,s^{-1}}$ criteria. These constitute a reference period with no drying of air for any of the instruments. In May during period 2, the inlet air for one of the Li-Cor 7200 instruments (Li72b) was dried using a Nafion dryer. In period 2, because of more rain events, 1381 high-quality 10-min values were available.

The latent heat fluxes from the two Li-Cor 7200 instruments (Li72a and Li72b) and one of the Li-Cor 7500 instruments (Li75a) are compared (Fig. 4a) to the latent heat flux measured by the other Li-Cor 7500 instrument (Li75b) for period 2. The comparison of the two Li-Cor 7500 instruments (black crosses) shows systematic differences of less than 2%. This reflects instrumental uncertainty and a different sampling of the smallest-scale scalar fluctuations by the different sensors.

A comparison of the undried enclosed-path Li-7200 instrument (Li72a) to the open-path Li75b (blue circles) showed losses of latent heat flux for this period of about 9% when using enclosed-path systems (similar percentage losses were found for both Li72a and Li72b for period 1). This loss of flux mainly occurred for frequencies above about 0.3 Hz according to cospectral analysis (not shown here). This loss of flux likely results from damping of fluctuations in tubing. The comparison of the latent heat fluxes from the dried Li72b instrument to the Li75b latent fluxes (red dots) shows that the Nafion dryer worked well to reduce the latent heat fluxes to nearly 0 (less than 1% of the Li75b fluxes in the mean).

From linear fitted expressions of the corresponding measured CO_2 fluxes from period 2 (Fig. 4b) it is first noted that there was essentially no difference in CO_2 flux between the two Li-Cor 7500 instruments (less than 1% systematic difference). Comparing the two Li-Cor 7200 instruments to one of the Li-Cor 7500 instruments shows that both the dried and undried sensors have a systematic loss in measured CO_2 flux of about 6%–7%. Thus, the dried CO_2 signal (red dots) and undried CO_2 signal (blue circles) agree equally well with the open-path system. For the CO_2 flux, a cospectral analysis showed that losses of flux took place over a large range of frequencies above 3/1000 Hz. Most notable was, however, that for the Li72b instrument, there was no mean flux contribution for frequencies above 0.7 Hz, where also spectral variance of the CO_2 signal was substantially reduced for enclosed-path instruments compared to open-path instruments. Some of the flux loss could be corrected using several of the approaches previously mentioned (Moore 1986; Hicks and McMillen 1988; Horst 1997; Massman 2000), but this would not affect our main results concerning the effects of drying or the effects from sea salt on the windows of the instruments.

The difference between the two enclosed-path sensors is very small. In Fig. 5, the measured CO_2 fluxes from the dried Li72b are directly compared to the fluxes from the undried Li72a instrument. This reveals that the two measured fluxes (dried and undried) agree very well, with a systematic difference of less than 2%. Only a few 10-min flux values stand out from the rest. Attribution of

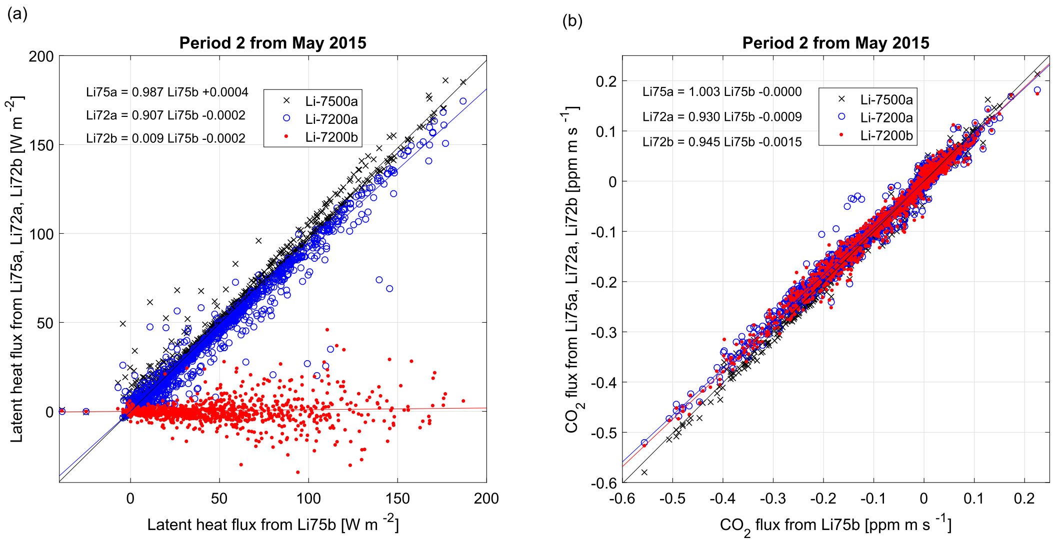

FIG. 4. A comparison of measured (a) latent heat flux and (b) CO_2 flux between the Li75b instrument and the other three instruments for period 2 when a Nafion dryer was installed on one of the Li-Cor 7200 instruments (Li72b). A comparison of the two Li-7500 instruments is shown (black crosses). A comparison of fluxes between the undried Li-7200 without a mounted Nafion dryer and one of the Li-7500 instruments is shown (blue circles). A comparison of the CO_2 fluxes with the dried Li-7200 to the same Li-7500 (red dots). Three fitted lines are included with the data in the corresponding color scheme, and the fitted expressions are given in the upper left of each plot.

the cause of these data would require further analysis, but it does not influence our main results in any way.

Box plots of the difference in measured CO_2 flux between the Li75b instrument and the other three instruments for periods 1 and 2 corroborate the results of small changes between periods (Fig. 6). The light gray boxes on the left show the comparison of the two Li-Cor 7500 instruments with no real change of median value in between the two periods but a slightly larger spread of the variations for period 2. Similar results are shown for the differences between the Li72a and Li75b fluxes (white boxes) and for Li72b and Li75b flux differences (dark gray boxes). The increase in spread of the differences in period 2 is not exactly understood.

Nevertheless, the systematic differences between instruments are relatively small in terms of differences between instruments (%), and the residual difference between the Li75b fluxes and the measured fluxes from the other three instruments is closer to being Gaussian than the CO_2 fluxes themselves from any single instrument. We can therefore rely on standard two-sample t tests for the change of mean values of these difference time series.

The mean CO_2 flux from period 1 is about -0.005 and about $-0.067\,\mathrm{ppm\,m\,s^{-1}}$ for period 2 (Table 2). It is reported in columns 2 and 3 (along with the mean difference after subtracting the Li75b flux). The change in mean for the difference time series between period 1 and period 2 is also given in column 4. Because of the high number of available data (more than 1000 10-min values) these rather small changes were found to be statistically significant at more than a 95% confidence level according to the t tests, but the largest change observed is for the

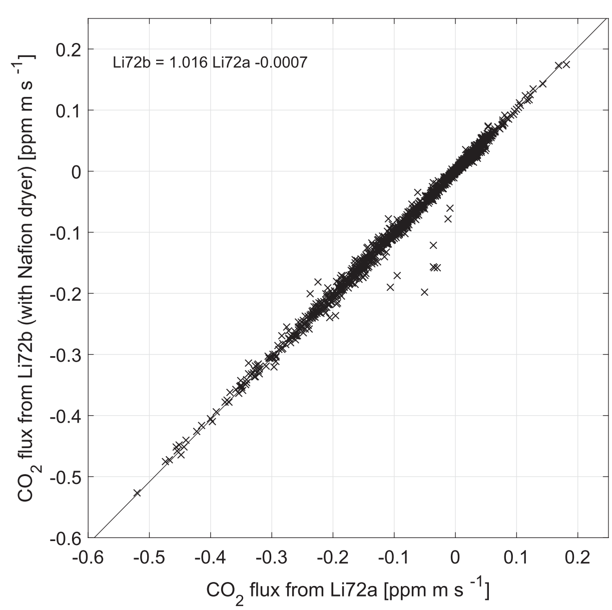

FIG. 5. A direct comparison of measured CO_2 flux from the undried Li-Cor 7200a instrument and the Li-Cor 7200b instrument with a Nafion dryer during period 2. The data (black crosses) and a linear fit to the data (black line) are shown. The fitted expression is also given in the upper-left corner.

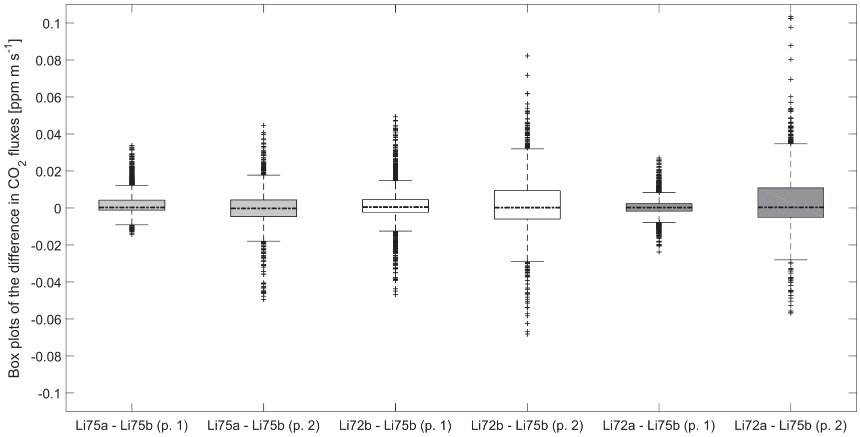

FIG. 6. Boxplots of the difference in measured CO_2 flux between the Li75b instrument and the other three instruments for period 1 (p.1) and period 2 (p.2). In period 2 a Nafion dryer was mounted on one of the Li-7200 instruments (Li-72b). The light gray boxes show the comparison of the two Li-7500 instruments. The white boxes show the comparison of the Li-7200 instrument with a Nafion dryer installed during period 2. The dark gray boxes show the comparison of the Li-7200 instrument without a Nafion dryer (Li72a). The median value is marked (dash–dotted line), and the boxes mark the 25th and 75th percentiles. Outliers are drawn as plus (+) signs if they are larger than Q3 + 1.5(Q3 − Q1) or smaller than Q1 − 1.5 (Q3 − Q1), which define the whiskers of the data. Here Q1 and Q3 are the 25th and 75th percentiles, respectively.

Li72a instrument without a Nafion dryer. This change is also only about 50% larger than the difference noted between the two Li-Cor 7500 instruments; therefore, it can be considered small. The change for the Li72b instrument with a mounted Nafion dryer in period 2 was even smaller. Therefore, we can conclude that drying the sample air does not alter the CO_2 signal very much.

2) ÖSTERGARNSHOLM

A similar test of the effects of drying the air for one Li-Cor 7200 instrument was also carried out at Östergarnsholm. In Fig. 7a the latent heat flux from Li72a without a Nafion dryer (blue) and Li72b with a Nafion dryer (red) is shown as a function of measured latent heat flux from a Li-Cor 7500 instrument. Only data from the open sea wind sector are used, and data with the same choice upon the variance of RSSI values ($\sigma^2_{RSSI} < 0.001$) as previously used for the Marsta data are shown as dots. These data still showed some scattered values, and data with circles are used for the stricter threshold value ($\sigma^2_{RSSI} < 0.00033$), corresponding to a stricter selection of data. The stricter threshold is used here to establish a relationship for the most reliable data (as indicated by RSSI). The less strict threshold value can still, however, be considered useful to provide an acceptable data quality in many contexts. If it is important for an application to retain a long continuous time series record, a compromise may have to be taken to find the most suitable threshold for the specific purpose and circumstance.

The linear fits to the highest-quality data show a similar result as in Marsta with a systematic loss in latent heat flux for the enclosed-path Li72a instrument. This loss is here seen to be somewhat larger (of about 29%), but the range of measured fluxes is also recognized as lower, between −10 and 50 W m^{-2}, at Östergarnsholm in comparison to Marsta, where it was between −20 and 190 W m^{-2}. The number of data is also fewer (only 58 data of the highest quality), which limits the possibility to assess with certainty the amount of systematic loss of latent heat flux during this experiment. It is nevertheless clear that the results are qualitatively similar for Östergarnsholm and Marsta. The amount of flux loss

TABLE 2. Statistical summary of the experimental field test with and without a Nafion dryer mounted on one of the Li-7200 instruments in period 2. From period 1 in April 2015, 2044 high-quality data (10-min values) were available and 1381 high-quality data were available from period 2 in May 2015 when the Nafion dryer was mounted on Li-7200b. Here change is defined as the difference in flux between periods 1 and 2 after subtracting the Li75b flux.

Name	Mean CO_2 flux (− Li75b flux) period 1 (ppm m s^{-1})	Mean CO_2 flux (− Li75b flux) period 2 (ppm m s^{-1})	Change (ppm m s^{-1})
Li75a	−0.0039 (0.0021)	−0.0672 (−0.0002)	−0.0023
Li75b	−0.0060	−0.0669	
Li72a	−0.0055 (0.0005)	−0.0631 (0.0038)	0.0033
Li72b	−0.0048 (0.0012)	−0.0648 (0.0022)	0.0010

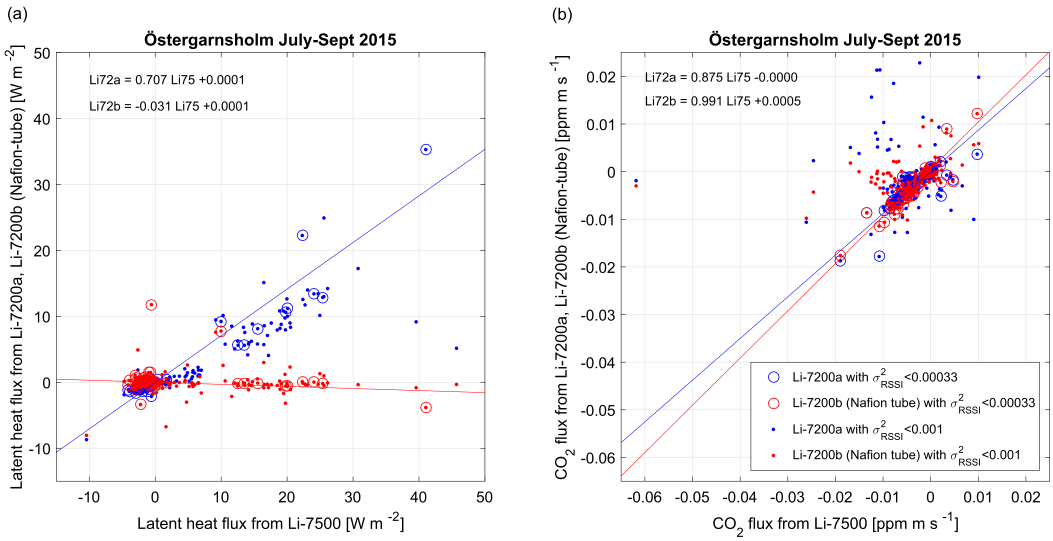

FIG. 7. A comparison of measured (a) latent heat flux and (b) CO_2 flux between a Li-7500 instrument and two Li-7200 instruments at the Östergarnsholm site. A Nafion dryer was mounted on one of the Li-7200 instruments (Li72b). Data marked with dots denote a selection criterion for the variance of RSSI to be less than 0.001. Data with circles correspond to a stricter limit of about one-third of that. Data from Li72a without a Nafion dryer (blue) and data from Li72b with a Nafion dryer (red) are shown. Two fitted lines are included for the most high-quality data using the same color scheme, and the fitted expressions are given in the upper-left corner of each plot.

may depend on a number of factors influencing the amount of covariance at short time scales. Some of these factors are wind speed, measurement height, and difference in surface roughness between Marsta and Östergarnsholm. From Fig. 7a it is also clear that the Nafion dryer worked well to remove water vapor flux. The latent heat flux was less than 4% for Li72b in comparison to the fluxes measured by the Li-Cor 7500 instrument.

The measured CO_2 flux from Li-7500 was compared to the fluxes from the dried and undried Li-Cor 7200 instruments (Fig. 7b) with the same symbols and color scheme. The result without drying the air (Li72a) indicates systematic smaller CO_2 fluxes of about 14% for the most high-quality data by the enclosed-path system. That result can be compared to the Li72b results, which include drying of the air, which show only a slight systematic reduction (less than 0.1%). Given the small number of data, it is difficult to clearly assess the amount of systematic reduction, or whether there is a reduction in CO_2 fluxes at all.

To test the significance of our preliminary conclusions, we carried out a statistical test also for the Östergarnsholm data. In Table 3 a statistical summary of the experiment with mean CO_2 fluxes of the three instruments is listed in column 1, which is noted to be small, on the order of 10^{-3} ppm m s^{-1}. The mean flux values for the two Li-Cor 7200 instruments are also seen to be very similar, differing by less than 2% from each other. From Fig. 7b we also note that the variation in measured fluxes is between about -0.020 and 0.014 ppm m s^{-1} for the most high-quality Östergarnsholm data. This can be compared with period 2 in Marsta, where the range of data is between -0.6 and 0.25 ppm m s^{-1}; thus, much more variable fluxes were observed at Marsta. The lower variability also made the data reasonably well approximated by a Gaussian distribution even without forming a difference time series by subtraction of a measured reference time series. Therefore, a two-sample t test could be considered here to directly test the change in the mean flux between the different instruments. In column 3 of Table 3, we listed both the difference in mean CO_2 flux between the Li-Cor 7500 instrument and the undried Li72a, which is larger, and the 10-times-smaller difference between the dried and undried Li-Cor 7200 instruments. Neither of these differences was found by the t test to be statistically significant. The difference in mean flux value between dried and undried Li-Cor 7200 instruments was significant only at a 4% confidence level. The larger difference between the Li-Cor 7500 and the undried Li-Cor 7200 was significant at a confidence level of 49%, which we consider too low to be truly conclusive.

c. *Will measured CO_2 fluxes be affected by sea salt contamination on the windows of instruments?*

During measurement period 4 in June 2015 at Marsta, some data were collected when the Li-Cor 7200 instruments (with and without Nafion dryer) were subjected to spraying of a saline solution on the windows of

TABLE 3. Statistical summary of the experimental field test with and without a Nafion dryer mounted on one of the Li-7200 instruments at the Östergarnsholm site. There were 58 high-quality data remaining when using the selection criterion $\sigma^2_{RSSI} < 0.00033$ and using data only from the undisturbed open sea wind sector.

Name	Mean CO_2 flux (ppm m s^{-1})	Mean CO_2 flux − Li72a flux (ppm m s^{-1})	Significant diff
Li7500	$-4.34\ 10^{-3}$	$-0.51\ 10^{-3}$	No (49%)
Li72a	$-3.83\ 10^{-3}$		
Li72b	$-3.78\ 10^{-3}$	$0.05\ 10^{-3}$	No (4%)

the instruments. This was used to test the hypothesis that hygroscopic deposits on the instrumental windows can lead to faulty and enhanced CO_2 flux estimates. In that case, this effect could be part of a possible explanation for the sometimes reported order-of-magnitude difference of fluxes in comparison to typical bulk formulations for air–sea exchange.

First, we compared the measured CO_2 fluxes during period 3 (Fig. 8a), which preceded the sea salt experiment and used a setup similar to the one in period 2. The main result is similar with less than 3% systematic difference between the two Li-7500 instruments and 5%–7% lower fluxes for the enclosed-path sensors in comparison to one of the Li-Cor 7500 instruments. The variation of measured fluxes for period 3 is larger in June than the other periods with 10-min flux values between −0.65 and 0.35 ppm m s^{-1}. This is interpreted to be caused by environmental changes on the surrounding crop fields. Choosing a period close to the reference period when the sea salt experiment was conducted ensures that changing environmental factors would be minimal.

Second, the measured CO_2 fluxes from the sea salt experiment in period 4 are compared between instruments (Fig. 8b). The Li-Cor 7500 instruments compared very well for this limited dataset of 47 high-quality data points (with $\sigma^2_{RSSI} < 0.001$) differing less than 1% from each other. The undried Li72a, which during this period was subjected to salt contamination on the instrument windows, showed systematic fluxes 4% higher than the Li-Cor 7500 instruments. This is an important change in behavior of the data in comparison to the observed typical lower flux values for the enclosed-path sensors. For Li72b with an installed Nafion dryer, this change of behavior is not observed. It still gives about 9% reduced CO_2 fluxes in comparison to the Li-Cor 7500 instruments. Apparently using the Nafion dryer in this case gave a reduced influence from the effects of hygroscopic deposits, although the number of available data is low. Comparing the 4% higher fluxes to the 9% lower fluxes would suggest a possible effect of about 13% enhanced fluxes as a result of salt contamination for the experiment. It should be noted that 13% on 0.3 ppm m s^{-1} (estimate of the median absolute flux value) corresponds to roughly 0.04 ppm m s^{-1}, which indicates that errors resulting from salt contamination needs consideration on sites with smaller fluxes. Over

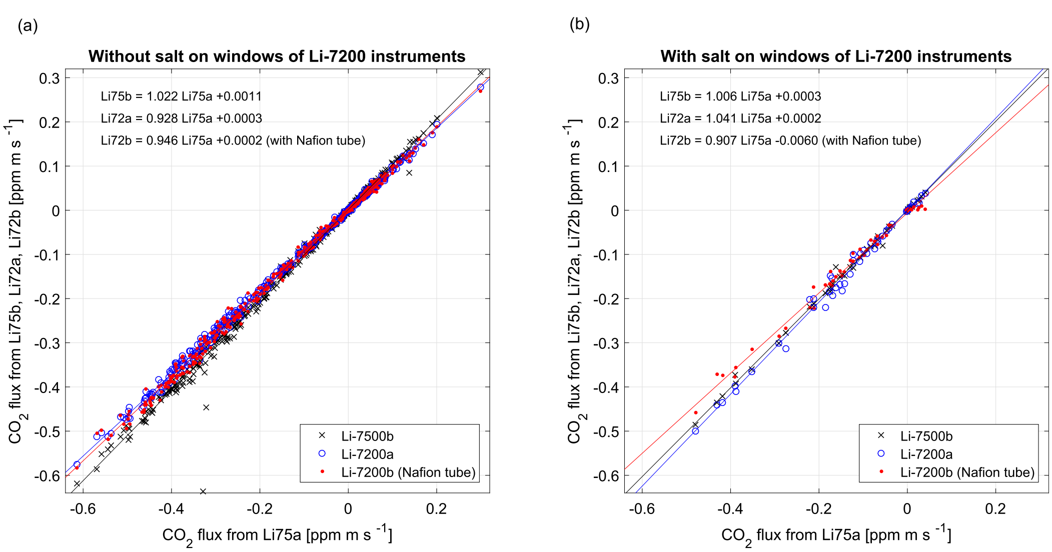

FIG. 8. A comparison of measured CO_2 fluxes between the Li75a instrument and the other three instruments under conditions (a) without salt and (b) with salt. A comparison of the two Li-7500 instruments is shown (black crosses). A comparison of fluxes between the undried Li-7200 without a mounted Nafion dryer and one of the Li-7500 instruments (blue circles). A comparison of the CO_2 fluxes with the dried Li-7200 to the Li-7500 (red dots). Three fitted lines are included with the data in the corresponding color scheme, and the fitted expressions are given in the upper-left corner of each plot.

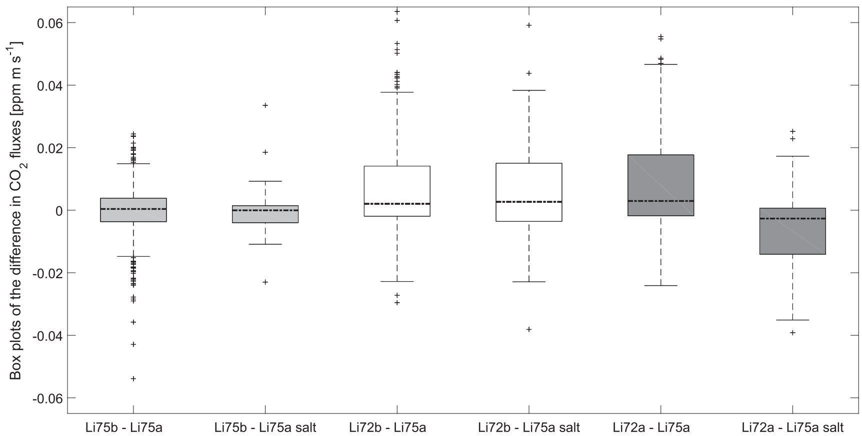

FIG. 9. Boxplots of the difference in measured CO_2 flux between the Li75a instrument and the other three instruments for two different periods without and with salt on the windows of the Li-7200 instruments. The light gray boxes show the comparison of the two Li-7500 instruments. The white boxes show the comparison of the Li-7200 instrument with a Nafion dryer installed (Li72b). The dark gray boxes show the comparison of the Li-7200 instrument without a Nafion dryer (Li72a). The median value is marked (dash–dotted line), and the boxes marks the 25th and 75th percentiles. Outliers are drawn as plus (+) signs if they are larger than Q3 + 1.5(Q3 − Q1); those smaller than Q1 − 1.5(Q3 − Q1) are drawn as whiskers of the data. Here Q1 and Q3 are the 25th and 75th percentiles, respectively. There are also a few outlier values for the period with no salt that lie outside the interval shown.

the open ocean, the magnitude of CO_2 fluxes is typically an order of magnitude lower than for land-based studies with latent heat fluxes being roughly comparable. This indicates that also small absolute errors should be a concern for ocean studies.

Box plots of the difference in measured CO_2 flux between one of the Li-Cor 7500 instruments and the other three instruments (Fig. 9) for period 3 and period 4 (which is denoted as the ‘‘salt’’ period) was used to illustrate the difference in behavior in the presence of salt. From the light gray boxes on the left, the two Li-Cor 7500 instruments are compared and a slight reduction in variance is observed for period 4, but this change is rather small and not very conclusive, as the number of data in period 4 is only 47 high-quality data compared to 428 10-min values for period 3. The median marked by the dashed–dotted line does also not change very much. For period 4 it is noted that some skewness is observed with more values less than the median value than above in the box (representing the 25th and 75th percentiles, respectively), but this is also not a very large change given the limited number of data in period 4. The white boxes show the result for the Li72b instrument with a Nafion dryer and here also the distributions do not change very much between the two periods. For the dark gray boxes on the right, which show the result for the undried Li72a instrument, the difference between the periods is larger with a change both in median value and a shift in the distribution. For period 3 the difference between the undried Li72a CO_2 fluxes and the Li75a fluxes is somewhat skewed so that more values are positive because of the larger uptake values of CO_2 measured at the Li-Cor 7500 instrument. In period 4 with hygroscopic deposits on the Li72a instrument windows, the distribution is shifted so that more negative values than positive values are observed because the higher uptake values of CO_2 are measured by the enclosed-path sensor.

A statistical summary of our sea salt experiment (Table 4) corroborates the results about the effect of salt. It is directly seen from column 4 that the change in the mean flux behavior for Li72b with a Nafion dryer is only 0.0001 ppm m s^{-1}, which is a 9-times-smaller change than between the two Li-Cor 7500 instruments (which was not subjected to salt contamination). For the Li72a instrument without drying of the air, the effect of salt contamination was much larger with a change of 0.0139 ppm m s^{-1}. This is a factor-of-15.4-times-larger change than for the two Li-Cor 7500 instruments. Although we have some observed skewness in the distributions, a two-sample t test applied to these different situations was done. For the undried Li72a instrument, the change was then found statistically significant at a confidence level of 99% (column 5 in Table 4), providing a strong argument that salt contamination can lead to enhanced CO_2 fluxes. The change between the

Table 4. Statistical summary of the experimental field test with and without salt on the windows of Li-7200 instruments. In this field experiment from June 2015, there were 428 high-quality data (10-min values) available before a saline solution was sprayed on the windows and 47 high-quality data with salt-covered windows remained.

Name	$\overline{CO_2}$ flux (− Li75a flux) without salt (ppm m s^{-1})	$\overline{CO_2}$ flux (− Li75a flux) with salt (ppm m s^{-1})	Change (ppm m s^{-1})	Significant change
Li75a	−0.1155	−0.1327		
Li75b	−0.1169 (−0.0014)	−0.1332 (−0.0005)	0.0009	No (28%)
Li72a	−0.1069 (0.0086)	−0.1380 (−0.0053)	0.0139	Yes (99%)
Li72b	−0.1090 (0.0065)	−0.1264 (0.0064)	0.0001	No (3%)

two Li-Cor 7500 instruments for the two periods was smaller and statistically significant only at a low confidence level of 28%, indicating no real significance. The Nafion-dried Li72b also had only a very small change that was completely insignificant (significant only at a 3% confidence level). These levels of confidence should be interpreted carefully because of the observed skewness in the distributions and that the number of data is relatively few (<50), but they show that some issues of salt contamination can exist when measuring CO_2 fluxes.

4. Summary and conclusions

To answer the question of whether drying the sampling air is important for measured CO_2 fluxes, field data were collected and analyzed from one agricultural site, Marsta, and one marine site, Östergarnsholm. The conclusion from the agricultural site was that no important change of CO_2 flux as a result of the drying of air was found. These conclusions are certain, as they are based on a fair amount of high-quality data (more than 1300 10-min values). There was, however, a systematic loss of flux in enclosed-path sensors of about 6%–7% for CO_2 and 9% for the latent heat flux in comparison to two open-path sensors, which only differed about 1% for CO_2 and 2% for latent heat fluxes. The underestimation of the enclosed-path sensors was partly from losses of flux at high frequencies (above 0.7 Hz), but some flux loss for CO_2 was found to take place also over a broader range of turbulent scales for frequencies above 3/1000 Hz. Further analysis of spectra and cospectra in varying atmospheric conditions would be required to gain more insights but was considered beyond the scope of the present study.

At the marine site, qualitatively similar results were reached with undried and dried enclosed-path sensors differing by less than 2%, and no statistically significant difference (only 4%) was found for the mean CO_2 flux value. The reduction in latent heat flux was found to be larger compared to the Marsta dataset, but the range of measured fluxes was smaller and the number of data points of the highest quality were fewer (<60). This limited the possibility to assess with certainty the amount of systematic flux loss from the Östergarnsholm dataset.

The recommendation for how to best measure CO_2 fluxes needs in our opinion to be different for different environmental conditions. In situations without salt contamination, our study concludes no clear effect on measured CO_2 fluxes from the presence of water vapor as long as instrument windows are kept clean. Thus, there is no need for extra dryer equipment in such situations. This eliminates the obvious drawback of placing a dryer for the intake airstream: that another instrument would then be needed to measure the latent heat flux. It also reduces the spectral attenuation that can be expected from using extra tubing.

According to our study, the salt contamination issue and the flux loss issue mainly at high frequencies are the two important issues that should be considered during the planning phase of an experiment. Cospectral flux loss is reduced using open-path sensors. In our study more high-quality data were retained when using open-path sensors in comparison to enclosed-path sensors. At sites where no obvious risk of optical contamination exists, a preliminary recommendation is to use open-path sensors for monitoring CO_2 fluxes.

For our land-based study, we found an effect of the salt-promoted cross sensitivity that altered the CO_2 fluxes by approximately 13%. This bias was statistically significant. On sites with small fluxes, the magnitude of absolute errors that this 13% change corresponds to is important, and several open ocean experiments (Miller et al. 2010; Landwehr et al. 2014; Blomquist et al. 2014) have shown order-of-magnitude differences. Using a Nafion dryer eliminated the influence from the effects of hygroscopic deposits on the instrument windows for our studied enclosed-path sensor, but the number of available data is admittedly low.

In the short-term application of infrared gas analyzers (IRGAs) in environments prone to sea salt, we support the conclusions from Miller et al. (2010); Landwehr et al. (2014) and Blomquist et al. (2014) that drying the air is to be recommended when measuring CO_2 fluxes. We would for the future also recommend feasibility studies

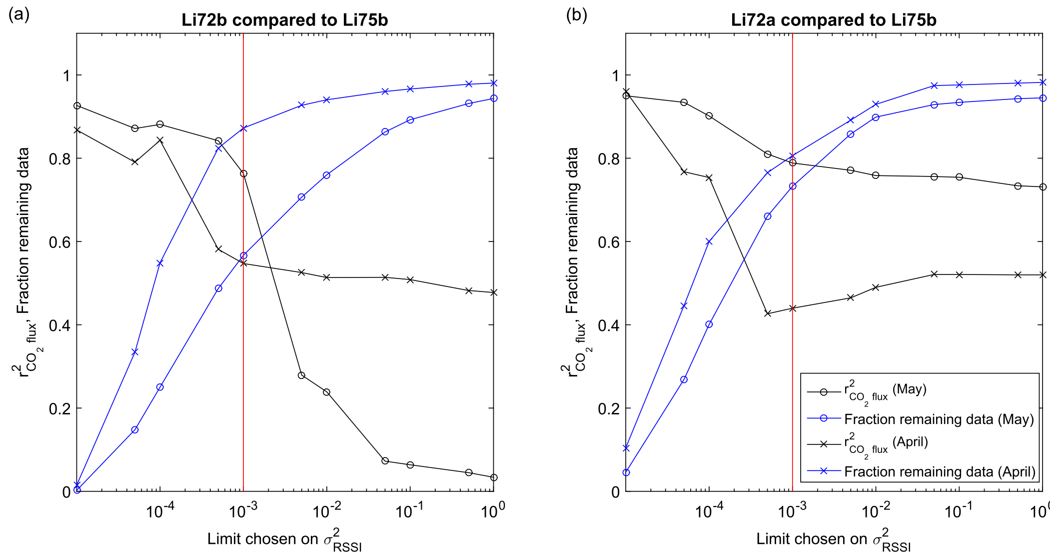

FIG. A1. The squared correlation coefficient for the CO_2 flux (black) and the fraction of remaining data (blue) are shown as a function of different threshold limits for σ^2_{RSSI}. The result for (a) Li-Cor 75a and Li-Cor 72b and (b) Li-Cor 75a and Li-Cor 72a. Data from April 2015 (lines with crosses) and May 2015 (lines with circles) are indicated. The threshold limit $\sigma^2_{RSSI} = 0.001$ is denoted (vertical red line).

for new instruments to include self-cleaning mechanisms or other ways for removing hygroscopic deposits from instrument windows. This would be a preferred option in comparison to using dryer equipment, since from our study we conclude no effect on measured CO_2 fluxes from water vapor itself. Only the combination of salt and water vapor showed a clear effect on measured CO_2 fluxes. We recognize that currently with the available measurement technology, drying the intake air may be the best practical option for ocean flux measurement studies of CO_2.

Regarding the issue of assessing the effects from water vapor and salt contamination separately, it may be important to reiterate a couple of things that make this study different from previous studies. A main difference between our Marsta data and studies conducted over open or coastal oceans is that at Marsta, cleaning away the salt is 100% effective. For measurement at sea, even the clean instrument is exposed to the salty air, so the "cleanliness" may last only some seconds or minutes. Optical contamination has been discussed in some studies to probably not be the source of cross sensitivity (Blomquist et al. 2014) but rather the water vapor itself. This can appear contradictory to our results. Blomquist et al. (2014) also mention, however, the possibility that relevant contaminants could be somewhat resistant to removal by rinsing. We also focused here on the measured CO_2 fluxes rather than the mean CO_2 concentration, which in Kondo et al. (2014) and Blomquist et al. (2014) was shown to be influenced by water vapor. Further study of sensitivity in results to both the amount of hygroscopic deposits on lenses and the resistance to removal of salt from instrumental windows in various conditions may be needed. The presented dataset and analysis suggest, however, that salt contamination can be a significant issue, leading to biased CO_2 fluxes. Furthermore, water vapor itself without salt had no important effect on our measured CO_2 fluxes.

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APPENDIX

Exploring the Effect of Filter Methods and Thresholds

The squared correlation coefficient (r^2) for CO_2 fluxes between the Li-Cor 7200 and Li-Cor 7500 instruments in

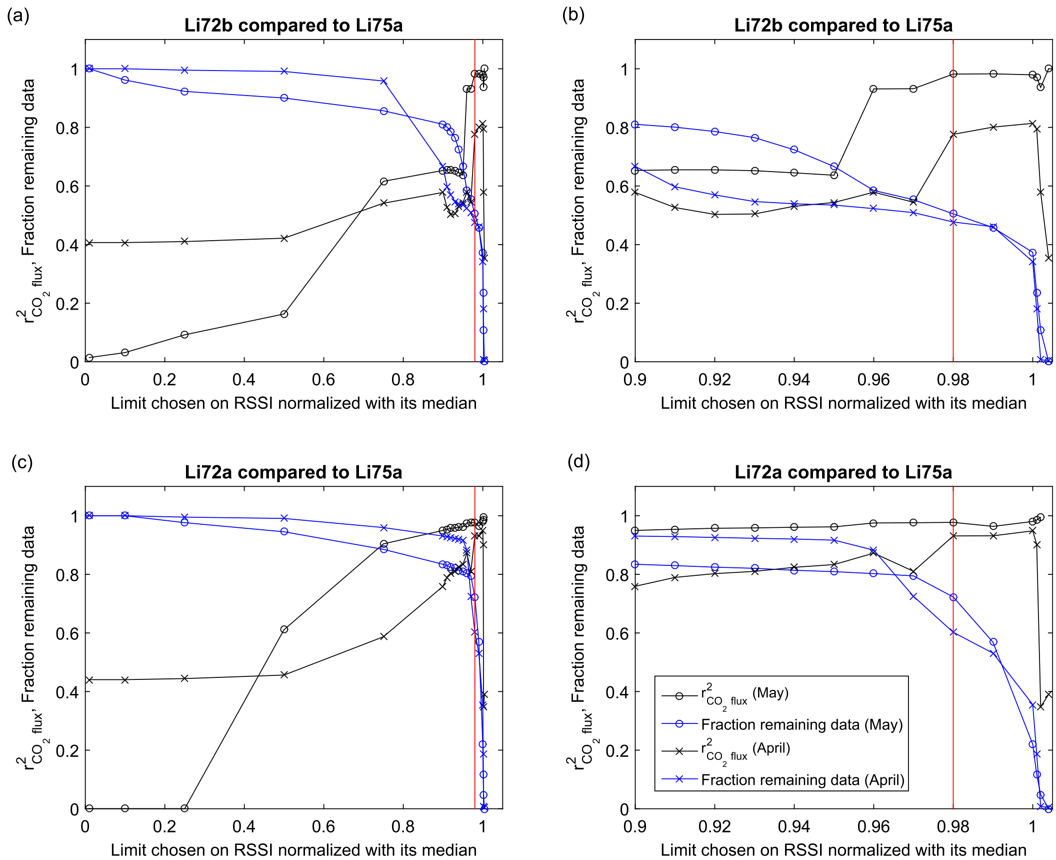

FIG. A2. The squared correlation coefficient for the CO_2 flux (black) and the fraction of remaining data (blue) are shown as a function of different threshold limits for RSSI values normalized by the median RSSI value ($RSSI/\widetilde{RSSI}$). Here the median is taken as the median of the measurement period. The result for the (a) Li-Cor 75a and Li-Cor 72b and the (c) Li-Cor 75a and Li-Cor 72a. (b),(d) Zoomed-in views on the range 0.90–1.01). Data from April 2015 (lines with crosses) and May 2015 (lines with circles). The threshold limit $RSSI/\widetilde{RSSI} = 0.98$ is indicated (vertical red line).

Figs. A1a and A1b show that the big drop in correlation during May occurred for the dried sensor Li72b (Fig. A1a). It did not occur for the undried enclosed-path instrument Li72a (Fig. A1b). This indicates the need for a strict threshold limit on σ^2_{RSSI} to obtain only high-quality data.

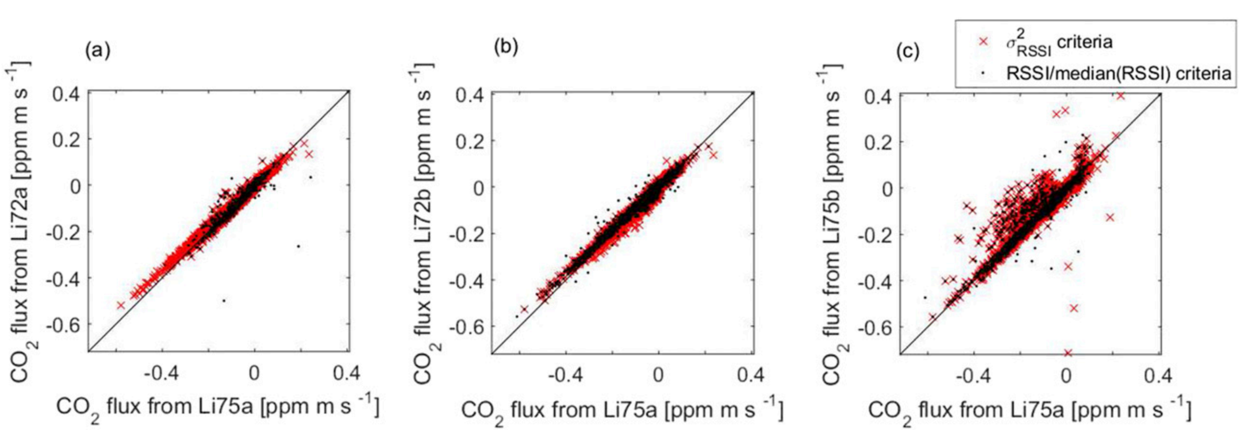

FIG. A3. The measured CO_2 flux from Li-Cor 7500a (both April and May data are included) is compared to the measured fluxes from (a) Li-Cor 7200a, (b) Li-Cor 7200b, and (c) Li-Cor 7500b. Data for the chosen threshold limit $\sigma^2_{RSSI} < 0.001$ (red crosses) and other selection criteria $RSSI/\widetilde{RSSI} > 0.98$ are denoted (black dots).

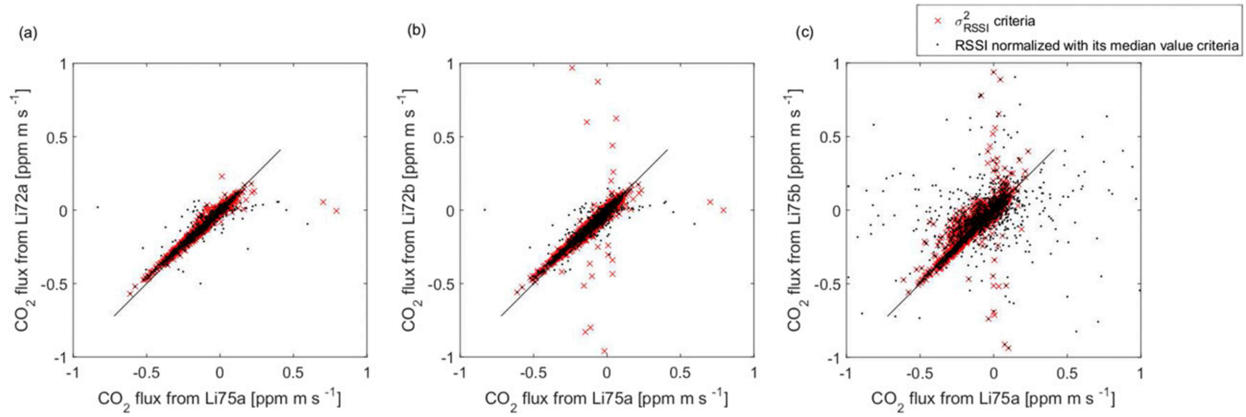

FIG. A4. The measured CO_2 flux from Li-Cor 7500a (both April and May data are included) is compared to the measured fluxes from (a) Li-Cor 7200a, (b) Li-Cor 7200b, and (c) Li-Cor 7500b. Data for the chosen threshold limit $\sigma^2_{\mathrm{RSSI}} < 0.05$ (red crosses) and another selection criterion based on $\mathrm{RSSI}/\widetilde{\mathrm{RSSI}}$ above a given limit so that the same number of data is selected (black dots).

As an alternative way to obtain high-quality data, we tested choosing different threshold limits on RSSI values normalized by the median RSSI value ($\widetilde{\mathrm{RSSI}}$) for each sensor. For the Li-Cor 7200b instrument, this approach required the limit to be chosen as $\mathrm{RSSI}/\widetilde{\mathrm{RSSI}} > 0.98$ if the r^2 value is above 0.75 in April (Fig. A2b). Between 199 and 277 more 10-min values (depending on which Li-Cor instruments were compared) were removed when the selection criteria based on $\mathrm{RSSI}/\widetilde{\mathrm{RSSI}}$ was used in comparison to that based on σ^2_{RSSI}.

The squared correlation coefficient between CO_2 fluxes measured by Li-Cor 7200b and Li-Cor 7500a (Fig. A3b) was high and equal ($r^2 = 0.98$) for both methods. Comparing the Li-Cor 7200a and Li-Cor 7500a fluxes (Fig. A3a), the squared correlation coefficient was lower ($r^2 = 0.93$) for the $\mathrm{RSSI}/\widetilde{\mathrm{RSSI}}$ criteria compared to the σ^2_{RSSI} criteria ($r^2 = 0.99$). Finally, both methods had trouble sorting out some outlier values found, especially on the Li-Cor 7500b instrument (Fig. A3c). The squared correlation coefficient between the two Li-Cor 7500 instruments was 0.90 for both methods (after ignoring the four most extreme outlier values).

A looser limit gives more scatter with both outliers above and below a 1:1 line as shown by Fig. A4, where a selection criteria $\sigma^2_{\mathrm{RSSI}} < 0.05$ was used for the recommended variance method. A variable limit c was set for the other method ($\mathrm{RSSI}/\widetilde{\mathrm{RSSI}} > c$) so that the same number of data was being selected in both methods. The full scatter is not shown by the chosen axis limits between −1 and 1, especially for the Li-Cor 7500 instrument comparison.

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